POTENTIAL DERMAL AND RESPIRATORY EXPOSURE TO ABAMECTIN DURING GREENHOUSE APPLICATIONS

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SUMMARY

Six different workers were monitored during seven applications of abamectin (Avid^R 0.15 EC) for potential dermal and respiratory exposure. In addition, the protective value of rainsuits and cloth coveralls was examined. Abamectin was applied to roses and chrysanthemums crops in semi-enclosed and fully enclosed greenhouses. Abamectin concentrations found in the workers breathing zone ranged from 0.1 ug/m^3 to 0.5 ug/m^3 . Total potential dermal exposure ranged from 15.41 ug to 6989 ug per gram active ingredient (ug/g A.I.) applied for unprotected applicators, and 0.86 to 8.00 ug/g A.I. for applicators protected by rainsuits and waterproof gloves. Penetration of spray material was estimated at 15 percent and 2.5 percent through cloth coveralls and rain suits, respectively. Field observations and data indicate that direct deposition rather than penetration through protective gear appears to account for most of the exposure to individuals protected by rainsuits and gloves. Foliage samples were collected at several intervals after each application and analyzed for dislodgeable abamectin residues to estimate initial depositions.

INTRODUCTION

The California Department of Food and Agriculture (CDFA) conducted a greenhouse pesticide applicator exposure study to gather information on pesticide applications and worker exposure data for a "generic" data base. In this context, "generic" or "surrogate" data are exposure monitoring data for pesticides that have been applied using comparable methods under similar conditions. The theory behind generic data bases contends that potential exposure is a function of the physical parameters of the application such as equipment used rather than the chemical properties of a pesticide. The concept and usefulness of generic data has been reviewed by several investigators and agencies (1,2,3,4). While there are data available on several types of field pesticide applications, very little data exists for workers who are exposed in a greenhouse or nursery environment.

The proposed data base will include exposure data from greenhouse applications of several commonly used pesticides. Thirty five workers were monitored during greenhouse applications of acephate, benomyl, captan, chlorothalonil, and fluvalinate. In addition, seven applications of Avid^R 0.15 EC (abamectin) were monitored under experimental use permits and the subsequent full registration. Potential exposure was estimated for workers utilizing several levels of protective gear. Data collected from passive dosimetry yielded information on potential dermal and respiratory exposure to applicators not protected, and protected by rainsuits and waterproof gloves. The protective value of cloth coveralls was also examined. The information and data collected from the abamectin greenhouse applications are presented in the following report.

MATERIALS AND METHODS

APPLICATION METHODS AND SITE CONDITIONS:

Potential dermal and respiratory exposure to six adult male workers were monitored during greenhouse applications of Avid^R 0.15 EC. A total of seven applications were monitored in three different types of greenhouses located in San Diego and Monterey counties. Applications were performed in fully or semi-enclosed greenhouses constructed with fiberglass panels, polyethylene sheeting, or a combination of the two materials. The commodities treated were chrysanthemums and roses propogated for cut flowers; all plants were grown in ground-level benches.

Abamectin was applied at the rate of 0.009 pounds active ingredient (lbs. AI) per 100 gallons of water. Several applications included the addition of a sticker-spreader or another pesticide in the spray tank. One hundred to 280 gallons of spray material were applied with commercial high volume spray equipment fitted with one of two types of spray wand. Roses were treated using a spray wand with a nozzle cluster comprised of three projections approximately three inches in length, each terminating in a single nozzle. Chrysanthemums were treated with a spray wand of a similar design except there were six rather than three nozzles. Applications ranged from approximately one to three hours in length.

Each individual was assigned a worker number which was used to identify samples and the resulting data. Workers wore the following protective gear and clothing during applications: rainsuit jacket and pants constructed from either neoprene coated fabric or waterproof nylon, hard hats or rainsuit hoods, faceshield or goggles, mid-forearm length waterproof gloves (neoprene, nitrile, or polyvinyl chloride), rubber boots, and a half-face respirator. New rainsuits were provided by the investigators for each monitoring period; gloves which were never used for abamectin applications were provided by the cooperating firm or the investigators.

For each application, the following data were recorded: individual's name, application site, date and time of application, length of application, spray rate and amount of active ingredient applied, temperature, observations and additional comments. A summary of application and site conditions is presented in Table I.

DERMAL EXPOSURE MONITORING:

Cotton glove liners, handwashes, and two types of dermal patches were employed to monitor dermal exposure. Monitoring procedures were modified from methods described by Durham and Wolfe (5), Davis (6), and Poppendorf and Leffingwell (7).

One type of patch, the "bi-layer" patch, was constructed of an outer cloth layer (7 ounce twill: 65 percent dacron polyester, 35 percent cotton) with an inner layer of twelve-ply gauze backed with food grade aluminum foil. Fabric was pre-extracted using ethyl acetate to remove substances that may interfere with analysis. Patch materials were housed in a foil-coated paper envelope which had a circular opening exposing 23.75 cm2 of media. Envelopes were constructed with the foil coating facing outward to repel spray material and minimize absorption through the paper. Patch materials were fastened into the envelope with staples to prevent any movement or loss from the patch holder during the application. Bi-layer patches were attached to the rainsuit using waterproof vinyl tape. Residues found on both layers of the bi-layer patch were used to estimate the total amount of pesticide that would contact the body without protective clothing. The residue levels found on individual layers were used to investigate the potential protective value of cloth coveralls. Therefore, residues found on the gauze layer were assumed to be the amount of pesticide that would penetrate cloth coveralls and reach the applicator's skin (8).

The gauze patch was constructed in a similar fashion as the bi-layer patch except it was comprised of a single gauze layer (12-ply) backed by aluminum foil. Gauze patches were fastened to a long-sleeved undershirt and pants worn underneath the protective rainsuit. Safety pins and plastic fasteners were used to attach patches to the garments. Residue levels found on gauze patches were used to estimate the amount of pesticide that would reach the skin and be available for absorption if rainsuits and no undergarments were worn. Clothing protection factors may be applied to these values to estimate potential dermal exposure when rainsuits are worn with undergarments such as pants and shirts.

Bi-layer and gauze patches were placed in locations suggested in the United States Environmental Protection Agency (E.P.A.) exposure monitoring

guidelines (Appendix II) (4). Patches were attached in the following areas: front and rear of each thigh and lower leg, each bicep, front and rear of each forearm, right and left sides of the chest, and the upper and lower back. In addition, gauze patches were attached to the front and rear of the outer most layer of head gear. Care was taken to place the bi-layer patches on areas of the rainsuit where they would not interfere with the exposure to underlying gauze patches. At completion of the monitoring period, patches were removed from the rainsuit and under garments in sequential order. Patches were removed from the envelopes using clean forceps and placed in Patches from the following body parts were pre-labeled four-ounce jars. combined as matched pairs for analysis purposes: front shins, rear shins, front thighs, rear thighs, front forearms, rear forearms, biceps, right and left chest, upper and lower back, and head patches. Matched pairs of gauze patches were placed in the same jar and considered as one sample for analysis purposes. Bi-layer patches were first separated into their respective cloth, and gauze and foil layers then placed in two separate jars as matched pairs. Jars were sealed with aluminum foil, capped, and stored on dry ice (solid carbon dioxide) until analysis.

Potential dermal exposure to the hands was monitored using handwashes, and glove liners worn under the applicators' waterproof gloves. Handwashes were collected before and after the monitoring period using the "bag-rinse" technique described by Durham and Wolfe (5). Handwashes were also collected prior to any break period where the applicator removed his gloves. Applicators were instructed to wash their hands for one minute in 400 ml of surfactant solution (0.1 % sodium dioctyl sulfosuccinate) contained in a one-gallon Ziploc plastic bag. This procedure was repeated at each post-application sampling interval. Each wash was immediately poured into an amber 500 ml Nalgene bottle then stored on Dry Ice until analysis.

One hundred percent cotton glove liners were pre-washed in hot water to remove lint that might interfere with the analyses. Glove liners were worn for the duration of the monitoring period. At the end of the application, waterproof gloves were removed by a technician to minimize contamination of glove liners. The applicator was instructed to place his hands in a one gallon plastic bag, then the technician removed the glove liners using the plastic bag as a protective device. Both left and right hand glove liners were placed in one bag, sealed, then stored on dry ice until analysis.

RESPIRATORY EXPOSURE MONITORING:

Potential respiratory exposure was measured using a personal air sampler (Mine Safety Appliance, Fixt-Flo^R pump, Model 1) equipped with a media sampling train comprised of a glass fiber filter (Type AE, SKC # 225-7) in a closed cassette followed by a sorbent tube packed with XAD-4 resin (SKC # Special, 200 mg/400 mg). Filters and tubes were used to collect aerosol and vaporized spray material. The cassette inlet was placed in the workers' breathing zone and fastened in place by attaching the train to the rainsuit collar. The sampling train was connected with Tygon^R tubing to the pump which was worn on a belt outside the rainsuit. Flow rates were calibrated at 1.0 to 2.0 liters per minute (lpm) using a Kurz 540S mass flow calibrator immediately prior to the monitoring period and checked at the end of the monitoring period. Initial applications were monitored using pumps set at 2.0 lpm but flow rates dropped during the monitoring period. Therefore,

subsequent applications were monitored using pumps set at a lower flow rate to avoid this problem. The average of pre- and post-application flow rates was used to calculate abamectin air concentrations.

DISLODGEABLE FOLIAR RESIDUES:

Foliage samples were collected and analyzed for dislodgeable abamectin residues. Dislodgeable foliar residues are the pesticide residues found on both upper and lower leaf surfaces that may be dislodged by an individual contacting the foliage. Data were used to demonstrate that abamectin was applied and to estimate initial deposition levels. Foliage samples were collected using methods adapted from Gunther et al. (9) and Iwata et al. (10).

Foliage samples were collected using the following general scheme: two adjacent benches or rows were selected from an area of the greenhouse where the treatment was expected to begin. An area 15 meters in length was selected from each bench, flagged, and used for sample collection. Foliage from the first and last two meters of the bench were not sampled. Chrysanthemum and rose foliage were collected using a clean 2.54 cm diameter Birkestrand leaf punch fitted with a four-ounce glass jar. Twenty leaf discs were collected from the two adjacent sides of each bench. Each sample contained a total of forty leaf discs. Samples were collected immediately prior to the application and 1, 2, and 3 hours after treatment of the sampling sites. Triplicate samples were collected at each sampling interval. Samples were stored with ice and shipped to the laboratory for analysis.

Abamectin residues were extracted from leaf samples within 24 hours of collection to minimize losses of dislodgeable residues due to leaf penetration. Fifty milliliters of Sur-Ten solution (0.1% sodium dioctyl sulfosuccinate) were added to each foliage sample, then mechanically agitated for 30 minutes; this procedure was repeated twice. Then abamectin was extracted from the combined surfactant solutions with ethyl acetate. Complete methods for extraction and analysis are presented in Appendix I. Leaf material from each sample was retained after extraction to verify the total surface area by either counting the leaf discs or measuring the leaves on an area meter (Li-Cor Model 3100). Dislodgeable foliar residue results were converted to micrograms of residue per square centimeter of leaf surface (ug/cm²) taking into account both upper and lower leaf surfaces.

ANALYSES:

All chemical analyses were performed in the CDFA Chemistry Laboratory Services, Sacramento, California using methods for HPLC-fluorescence determination of abamectin (11, 12). Abamectin was extracted from samples using the appropriate solvent for each medium. Solvent extracts were concentrated then reacted with a reagent (N,N-dimethylformamide/acetic anhydride/1-methylimidazole) for one hour at 95-100°C to form the fluorescent abamectin derivative. The resulting solution was passed through a Sep-Pak silica cartridge, eluted with chloroform to a specified volume, evaporated to dryness, then redissolved in methanol in preparation for analysis by liquid chromatography. The abamectin derivative product was analyzed by reverse phase liquid chromatography using a Perkin-Elmer Series

4 chromatograph equipped with a fluorescence detector. The column used was an Altex ultra-sphere ODS 4.6 mm i.d. x 150 mm column operated at a temperature of 35° C. Abamectin was resolved under the following conditions: mobile phase, methanol-water (97:3); flow rate, 1.5 ml/min; excitation wavelength, 364 nm; emission wavelength 480 nm. Under these conditions, Abamectin B₁ had a retention time of 8.17 minutes and a minimum detectable level of 0.2 nanograms per sample. Complete analytical methods are presented in Appendix I.

RECOVERY PROCEDURES:

Recovery efficiencies were determined in the laboratory by fortifying media samples with abamectin standard solution and formulated material at three levels that would be expected in field samples. The mean recovery was 107 percent with a range of 99 to 115 percent. Storage stability of fortified samples was tested over a six-week period. No losses were noted except from the handwash samples; abamectin recoveries from handwashes ranged from 27 to 138 percent over the six week period without following a set pattern. Abamectin was not detected in blank samples.

Recovery studies were also conducted in the field. Tank mix samples were collected from each spray tank used during the monitoring period. A subsample from the first tank mix sample was used to fortify the five types of sampling media at three different levels (0.04, 1.0, 4.0 ug per sample); duplicate samples were prepared. One complete set of samples was fortified and immediately stored on dry ice. A second set of samples was fortified and exposed to a greenhouse environment with conditions similar to the treatment area for a time period equal to the application period. Shipping blanks were prepared for each set of samples. Sample results were used to verify initial concentations and to determine if losses occurred during the monitoring period.

RESULTS

Abamectin residue levels found on dermal and respiratory dosimeters are presented by worker identification number in Table II. Patch residue levels are given in micrograms of abamectin per sample which consisted of a matched pair of patches from each body area. Residue levels are given for the individual cloth and gauze layers of bi-layer patches, and for gauze patches. The value given for handwash data is the sum of residues found in all post-application handwashes.

The raw data was extrapolated to represent full body dermal exposure using standard body surface areas (Appendix II). The minimum detectable level stated in Table II was substituted in extrapolation calculations when abamectin was not detected in a sample. No abamectin was detected on the gauze patches (excluding head patches) worn by four of seven applicators. Abamectin was not detected on 19 of the 27 gauze patches worn by the remaining three applicators. In most cases, abamectin was detected on bilayer patches (Table II). The extrapolated data representing potential dermal exposure to each body area is presented by worker number and sample media type in Table III. The extrapolated data was normalized to determine the level of exposure in micrograms for each gram of active ingredient applied; data are presented in Table IV.

Total exposures were estimated using extrapolated data and normalized data (Tables III and IV). Potential dermal exposure to workers not protected or clothed (exposure"II"), and potential exposure to workers wearing rainsuits and waterproof gloves (exposure "III") were calculated. Total estimated dermal exposure based on abamectin levels found on external patch dosimeters ranged from 15.4 ug to 6984 ug for each gram of active ingredient applied. These estimates do not include the potential exposure to unprotected hands. Total estimated dermal exposure (excluding head region) for an applicator wearing a rainsuit and waterproof gloves ranged from 0.86 to 8.0 ug for each The head region was not included in these gram of abamectin applied. data was not available to calculate exposure to estimates because applicators wearing protective head gear. The mean total dermal exposure for individuals wearing different types of protective clothing is presented in Table V.

Potential dermal exposure to individuals wearing cloth coveralls and the protective value of coveralls were estimated using the residue levels found on the gauze and foil layer of external bi-layer patches. However, these estimates may not accurately reflect potential exposure because many of the patches became saturated with spray material during the monitoring period. The amount of spray material on a patch was determined using spray tank concentrations and patch residue data; estimates indicated that several patches were exposed to an excess of 7.5 ml each. Although other patches were theoretically exposed to less spray material, field observations found that both layers of bi-layer patches were damp with spray material. Apparently spray material was soaking through the cloth layer and was readily absorbed by the gauze layer which was acting like a wick. human skin does not act like a wick when exposed to liquids, it is unlikely that similar exposures would occur when applicators are wearing cloth coveralls. Therefore, caution should be used when interpreting bi-layer patch data to estimate potential dermal exposure and the protective value of cloth coveralls. Penetration of spray material through cloth coveralls was estimated at 4.6 percent to 41 percent; penetration through rainsuits was estimated at 0.05 percent to 5.4 percent (Table VI).

Abamectin air concentrations found in the worker's breathing zone ranged from 0.1 ug/m^3 to 0.5 ug/m^3 , if detected. Minimum detectable levels were either 0.1 ug/m^3 or 0.2 ug/m^3 depending on the application length (Table II). Potential respiratory exposure for applicators based on a breathing rate of 36.75 liters per minute for high heat, heavy work conditions (15) ranged from 0.41 to 2.98 micrograms per application. The use of respirators, which are required for workers mixing and applying abamectin, would decrease the potential respiratory exposure. Abamectin air concentrations found during this study were lower than the respiratory exposure limit of 0.04 ug/m^3 suggested by the Merck and Company, Incorporated (16). Permissible exposure limits or thresold limit values have not been extablished for abamectin.

Abamectin residues were found on hand dosimeters (glove liners and handwashes) after three of the seven applications. Data collected from handwash samples should be interpreted with caution because recovery during laboratory storage stability studies ranged from 27 percent to 138 percent over a six week storage period without a noted trend. Handwash samples collected from applications 27 and 22 were in frozen storage for 2 and 3 weeks, respectively, prior to analysis. All other handwash samples were in

frozen storage for six weeks.

Mean dislodgeable foliar residue levels found in samples collected after all applications except #23 ranged from 0.006 to 0.017 ug/cm^2 . Dislodgeable residues found before and after application 23 ranged from 0.001 ug/cm^2 to 0.003 ug/cm^2 . A reduction in dislodgeable residue levels from samples collected over a three hour period was not observed (Table VII).

DISCUSSION AND CONCLUSIONS

The original study was designed to determine if dermal and respiratory exposure was linearly related to the spray rate (pounds active ingredient per 100 gallons of water) rather than the total amount of active ingredient applied. On several occasions two applicators sharing the same spray tank were monitored. This did not appear to be a problem at that time because the original study design addressed exposure based on spray rate. Subsequently all monitoring data was normalized to total amount of active ingredient applied per worker rather than the spray rate for comparison purposes. Therefore, the estimated exposures for individuals sharing spray tanks may not be accurate.

Applications 22 and 29, and 24 and 25 were performed simultaneously by different individuals working in the same greenhouse ranges. These workers were applying abamectin with individual spray wands attached to the same spray tank. The total amount of active ingredient applied per worker was estimated using the time length of each application. These estimates may not accurately reflect the actual amount of active ingredient applied per worker. Therefore, dermal exposure estimates based on normalized data for these applicators should be interpreted with caution (Table IV).

The study design also did not allow control over other variables such as type of spray wand used, application methods, commodity treated, and type of greenhouse treated. Many of these variables were difficult to control because they were dependent on the target pest and the pesticide used. For example, abamectin applications that were monitored consisted of treatments to two different commodities using two types of spray wands in several types of greenhouses. Consequently, the resulting monitoring data varied considerably between applications. Other investigators who had controlled many of these variables have also encountered problems with variability in exposure data from similar applications (13, 14).

In general, abamectin residues found on dosimeters attached under rain suits and worn under waterproof gloves were low or not detected. Glove liners were found to be easily contaminated by the worker. In one case, the worker participating in application 22 was observed touching his contaminated waterproof glove while wearing the glove liners. The glove liner was probably contaminated with abamectin at that time producing the low levels of abamectin that were found on the liners (Table II). In a real-life situation, hand exposure could conceivably be much higher because workers do remove their gloves during applications to move objects, fix equipment, etc.

In addition, substantial potential for exposure exists when the applicators removes protective clothing which is contaminated with spray material.

Although there were no incidents observed to explain the high levels of abamectin found on the glove liners worn during application 27, the high residue levels were probably due to direct contamination rather than penetration through waterproof gloves. This individual was wearing waterproof gloves that had been worn for other pesticide applications. However, contamination with abamectin from previous applications is unlikely because this pesticide was not registered for use in California during the study period. At this particular site, greenhouses were located over a large hilly area and several greenhouse ranges were treated during each of the applications. Each range was located in a different area; therefore, the applicator was required to drive a truck hauling the spray equipment to each location. We were unable to observe the applicator while he was driving to each site. During this period the applicator might have removed his waterproof gloves which would allow for substantial glove liner contamination if they had contacted the rainsuit or other items used during the treatment. This individual also performed application 23, but glove liner data was not available for comparisons. Since the glove liner residue levels from application 27 were unusually high when compared with data from the other applications, contamination of the sampling media prior to, during or after the application is suspected.

Abamectin levels found on external dosimeters varied considerably between applications. Field observations indicated that spray runoff from the plants and spray drift appear to account for the high levels of abamectin found on external bi-layer patches. Bi-layer patch dosimeters, primarily in the thigh and forearm regions, were frequently saturated with spray material. Preliminary calculations estimated that each saturated bi-layer patch was holding 5 to 8 ml of spray material to result in the abamectin levels found on these patches. Accurate protection factors for cloth coveralls could not be estimated using data collected from saturated patches. Therefore, the method employed to monitor potential exposure when cloth coveralls are worn does not appear to be adequate. During an actual application, cloth coveralls may also become saturated with spray material and not provide protection in the greenhouse environment.

The same individual performed applications 23 and 27 at the same greenhouses on different occasions. Although application 27 was one of the smaller applications both in duration and amount of active ingredient applied, the applicator experienced the highest exposure on external patch dosimeters. In addition, abamectin residues found on the outside of rainsuits after applications 23 and 27 were the highest levels found during the study. high level of exposure to external patches may be due to the nature of the treatments or this individual's work practices. Work practices and treatment methods were noted during most of the monitoring period. restraints required that the worker perform the application quickly then move on to the next site. Monitoring data indicates that the applicator was spraying more abamectin on himself than on the plants. Although high levels of abamectin were found on the rainsuit, no abamectin was detected on dosimeters worn under the rainsuit indicating the high degree of protection a rainsuit can provide.

Field observations found that in most cases, workers wear at least a shirt and long or short pants under the rainsuit. Several cooperators required workers to wear Tyvek $^{\rm R}$ coveralls under the rainsuit instead of, or in

addition to street clothes. The exposure estimates presented in Tables III and IV include potential abamectin exposures for applicators wearing protective gear (rainsuits and waterproof gloves). These estimates do not take into consideration the protective value of garments that may be worn under the rainsuit. Theoretically, the actual dermal exposure would be lower than the estimated exposures stated if clothing or coveralls were worn under the rainsuit. Potential dermal exposure for workers wearing under garments can be estimated using data collected from dosimeters worn under protective gear with the appropriate clothing protection factor.

In summary, field observations and exposure monitoring data indicates that abamectin spray material probably passes through openings in the garments rather than penetrating through the rainsuit or gloves. Abamectin was found primarily on patches located in the chest, back, forearm, and shin regions located under the rainsuit. Therefore, the spray material might have entered through the neck, cuff or leg openings. Incidental contamination also appears to account for residues found on several dosimeters. Fenske (14) examined the performance of several types of protective clothing using a fluorescent tracer. Similarly, he found that most of the exposure that occurred beneath protective clothing was near the sleeve and neck openings. He also found that hand exposures when wearing gloves were probably due to contamination during glove removal and handling.

TABLE I: Site Conditions and Application Methods for Abamectin Greenhouse Applications $^{2\!\mathcal{L}}$

Application		Plant Ht.	ay Material	Total	Applic Time	Type of	Greenhouse	Rain Suit Ivpe
L.D. No.	COMMOGICY	(Meters)	Applied (gallons)	ThatTiddy TW SdT)	(BYIIITES)	STEEL METER	241	
22	roses	1.5 - 2.4	200	0:02 <u>b</u> Z	195	three nozzle	fiberglass	rubber-coated fabric
23	chrysanthemums	0.6 - 1.0	200	0.0207	111	six nozzle	poly roof/	nylon w/polyurethane barrier
24	chrysanthemums	various	225	0.021	132	six nozzle	fiberglass	nylon w/polyurethane harrier
25	chrysanthemums	various	200	0.02	102	six nozzle	fiberglass	nylon w/polyurethane
26	chrysanthemums	1.0 and over	200	$0.05 \overline{p}$	91	six nozzle	poly house	nylon w/polyurethane
27	chrysanthemums	0.6 - 1.0	100	0.01	70	six nozzle	poly house	nylon w/polyurethane
29	roses	1.5 - 2.4	280	0.028 <u>b</u> Z	186	three nozzle	fiberglass	rubber-coated fabric
			. 2					
Spray Tank Additives -	22 - 23	0.6 lbs/100 ga	none orthene 0.6 lbs/100 gal, sticker/spreader					
	24 none 25 none							
	26 sticker, 27 sticker,	sticker/spreader sticker/spreader						
	29 none	1				٠		

3L Abamectin applied at the rate of 0.009 pounds active ingredient per 100 gallons water.

bL Formulated product supplied by registrant and used in accordance with experimental use permit.

Abennectin Residues Found on Greenhouse Applicator Dermal and Respiratory Dosimeters. TABLE II:

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Head	1	0.10	•	•	9	•	r	8. 5	1	•		_ `	, ,	3.5	5	20 01	9	E	2 83	£	2
Bicen	1.26	8.0	2	0.0	2	2	2	2	2	2			0.17	₹ 9)))	7.75	1 0	2 6	17.	E7 0	2
Forearm (F)	0.72	2	2	0.10	2	2	,0.07	2	2	2			0.T/	⊋ !	⊋ 9	70.7	÷	9 €	17.0	8	5
Forestta (B)	0.46	2	2	6.50	0.10	2	0.07	2	2	2			8.9	2	⊋ 5	3 5	2 9	2 6	77.71	3 5	6
Chest	0.20	2	2	2.20	2	2	0.03	2	2	2			₹ 5	0.0 !) (0.0	2 . 2	⊋ ii	2 6) E	3 5	<u> </u>
Back	2	2	2	1.8	٠. ک	0.20	2	2	2	2			8	2	2 !	i d	27.75	2 6	, r	, F	2 6
Thigh (F)	1.18	52.0	2	9.9	4.80	<u>ه</u>	2.30	2	2	o.3			8.9	o.	⊋ !	¥ 5	22.30	2 6	3 6	}	! €
F. (8)	E	Ø	£	21,70	09.0	2	0.10	2	2	0.05			2	2	2	K#.97	20.02	2 !	3 6	9 6	, S
Spin (F)	1 2	0.12	2	8	Ð	2	2.70	2	2	4.00	2	2	15.90	1.20	2 !	143.41*	* X X	2 9	17.5	⊋ ²	3 5
Shin (B)	0.62	包	2	64.00	11.69	2	0.50	2	2	0.20			0.50	2	2	139.40 4	*. 7.	⊋.	1.13	3	3
											1			Ē			1 20			0.99	
Handwash		2			2			2			₹			2			}				
Glove Liner		90.0			•			2			2			2	•		20.37	•	•	2	
)ems			- Am	-		0.2			0.1			0.2			0.5			NDS	
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(ug/sample)																					

a minimum detection level = 0.2 ug/m^3 minimum detection level = 0.1 ug/m^3

ND = not detected (less than minimum detected level)
"-" No sample
BC = bi-layer patch, residue found on cloth layer only.
BG = bi-layer patch, residue found on gazze and foil layers.
IG = gazze and foil patch attached to the applicators clothing under the rainsuit.
F = front
B = back

Dosimeters appeared to be saturated; estinated approximately 7.5 ml spray meterial was on each dosimeter.

TABE III: Abarectin Residues Found on Greenkouse Applicator Dermal Dosimeter, A Values Extrapolated to Represent Exposure to each Body Area 👱

Particularity: 22 23 24 24 25 25 25 25 25 25							•	(estin	ated m	CTOFTAINS	OI BVE		Der Doory	9					ا ا
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g/s samples with no detectable residues were assumed to have the minimum detectable level. b/s Based on body surface areas presented in EPA Exposure Assessment Cuidelines, Subdivision U (4).

"-" No sample

NA - Not available

EC = bi-layer patch, residue found on cloth layer only.
EG = bi-layer patch, residue found on gazze and foil layer.
EG = gazze and foil patch attached to the applicators clothing under the rainsult.
I = Total body exposure estimated for each patch type (excluding head).

II = Total estimated dermal exposure if no protective gear or clothing was worn (excluding hands).
III = Total estimated dermal exposure if a rainsuit and waterproof gloves were worn.

F - front

B - back

* Dosimeters appeared to be saturated; estimated approximately 7.5 ml of spray material was on each dosimeter

Absmectin Residues Found on Greenhouse Applicator Dermal Dosimeters, 3 Ratio of Exposure to each Body Area 5 par Gram of Avermectin Applied TARLE IV:

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Samples with no detectable residues were extrapolated using the minimum detectable level. Based on body surface areas presented in EPA Exposure Assessment Guidelines, Subdivision U (4). a/ Samples with no detectable residues were extrapolated using the minimum detectable level.

b/ Based on body surface areas presented in EPA Exposure Assessment Guidelines, Subdivision U (4).

c/ Estimate does not include hand exposures.

MA - Not available

BC - bi-layer patch, residue found on cloth layer only.

BC - bi-layer patch, residue found on gauze and foll layer.

BC - bi-layer patch, residue found on gauze and foll layer.

IG - gauze and foll patch attached to the applicators clothing under the rainsuit.

I - Total body exposure estimated for each patch type (exclude head).

II - Total estimated demal exposure if no protective gear or clothing was worn (excluding hands).

III- Total estimated dermal exposure if a rainsuit and waterproof gloves were worn. F - front

* Dosimeters appeared to be saturated; estimated approximately 7.5 ml of spray material was on each dosimeter.

TABLE V: Mean Dermal Exposure for Seven Greenhouse Applicators Wearing Several Types of Protective Clothing and Gear.

(in micrograms abanectin exposed per gram active ingredient applied)

Level of Protection	Mean, Standard Deviation 4/
Hands protected by waterproof gloves	3.81 ± 8.71 <u>b</u> /
Total estimated body exposure for each patch type (excluding head region):	
Bi-layer patch, cloth layer	814.4 ± 1834.0
Bi-layer patch, gauze layer	302.2 ± 757.3
Gauze patches	1.87 ± 1.01
Total estimated exposure if no protective gear was worn (excluding hands)	1118.0 ± 2593.0
Total estimated exposure if a rainsuit and waterproof gloves were worn	2.67 ± 2.46 <u>b</u> /

When no abamectin was detected, the equivalent of the minimum detected level was used in the calculations.

b/ Exposure data from six applicators.

Table VI: Estimated Percent Penetration of Abamectin Spray Material Through Cloth Coveralls and Rainsuits.

WORKER NUMBER	% PENETRATION ª/ CLOTH COVERALLS	% PENEIRATION b∠ RAINSUITS
22	9.9	4.4
23	12.3	0.5
24	4.3	3.7
25	6.0	5.4
26	5.9	1.9
27	41.0	0.05
29	22.0	1.7
MEAN + STANDARD DEVIATION	15.0 ± 13.0	2.5 ± 2.0

a/ Calculated using data from torso and limb bi-layer patches:

b/ Calculated using data from torso and limb bi-layer and gauze patches:

TABLE VII: Mean 2/ Dislodgeable Foliar Residue Levels of Abamectin Found After Greenhouse Applications

(in micrograms per square centimeter surface area)

Sampling Interval	22	23	APPLICATION 24,25	26	_27
Pre-Applic	ND/p/	0.001 ± 0.002	NDC/	NDp/	NDp/
l hour post application	0.011 <u>+</u> 0.001	0.002 ± 0.003	0.012 ± 0.006	0.011 ± 0.001	0.011 ± 0.001
2 hour post application	0.014 ± 0.0004	0.003 ± 0.001	0.016 ± 0.003	0.007 ± 0.001	0.011 ± 0.001
3 hour post application	0.013 ± 0.0001	0.001 ± 0.001	0.017 ± 0.002	0.006 ± 0.001	0.011 ± 0.001 <u>d/</u>

a/ Mean and standard deviation of triplicate samples, except where noted.

b/ Minimum detected level = 0.00009 ug/cm²

^{₫/} Mean and standard deviation of duplicate samples.

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APPENDIX I

ANALYTICAL METHODS FOR AVERMECTIN B1

SCOPE:

This method is a modification of Method No. 5004 of Merck Sharp & Dohme Research Laboratories for the HPLC-fluorescence determination of avermectin $B_1(1)$. It is applicable to the analysis of gauze and cloth patches, XAD-4 air tubes, glass fiber filters, cotton gloves, Sur-Ten handwashes and dislodgeable foliar residues.

PRINCIPLE:

The avermectins are extracted from the different matrices by suitable solvents. The solvent is evaporated and the fluorescent avermectin derivative is formed by reaction with N, N-dimethylformamide/acetic anhydride/1-methylimidazole reagent for one hour at 95-100°C. The reaction mixture is dissolved in chloroform and passed through a Sep-Pak silica cartridge. The eluant is evaporated to dryness and redissolved in methanol. The avermectin derivative is determined by reversed phase liquid chromatography.

REAGENTS AND EQUIPMENT:

Solvents (nanograde):

Acetonitrile Chloroform Ethyl acetate Methanol Toluene

Derivatization reagent: Mix in a test tube containing 0.6 ml acetic anhydride, 1.8 ml N, N-dimethylformamide and 0.4 ml 1-methylimidazole. This reagent must be prepared just before use.

Avermectin standard solutions

Sodium chloride

Sodium sulfate, anhydrous

Sur-Ten solution, 2% (dioctylsulfosuccinate sodium salt)

Glassware:

Boiling flasks

Glass filter funnels

Glass stoppered test tubes

Graduate cylinders

Luer syringes

Mason jars

Pipets

Separatory funnels

Apparatus:

Heating block or oil bath with temperature control

Gyratory shaker

Rotary evaporator

Rotators

Sonicator

Thermometers

Wrist-action shaker

Nylon acrodisc filters, 0.2 um

Sep-Pak silica cartridges

Equipment Conditions:

Liquid chromatograph: Perkin-Elmer Series 4 Column: 4.6 x 150 mm Altex ultrasphere ODS, 5um

Column temperature: 35°C

Mobile phase: 93% methanol, 7% water

Flow rate: 1.5 ml/min

Fluorescence detector: excitation wavelength- 364 nm emission wavelength- 480 nm

ANALYSIS:

Extraction Procedures:

A. Gauze and Cloth Patches

- 1. Add 50 ml methanol to sample jar containing patch.
- 2. Shake jar in wrist-action shaker for 30 min.
- Transfer 20 ml of the methanol extract to a boiling flask and evaporate to near dryness.
- 4. Transfer concentrated extract to a 15-ml glass stoppered test tube. Rinse boiling flask by sonicating with a few mls of methanol. Add rinsing to test tube.
- 5. Evaporate to dryness under N_2 at $50-60^{\circ}\text{C}$. Proceed with derivatization.

B. Filters and XAD-4 Tubes

- 1. Transfer filter or XAD-4 resin including plugs into a 5-ml vial.
- 2. Add 5 ml of toluene-acetonitrile (1+3) to the vial. Place vials in a mason jar and rotate for 30 min.
- 3. With a pipet, transfer 2 ml of the toluene-acetonitrile extract to a 15-ml glass stoppered test tube.
- Evaporate to dryness under N₂ at 50-60°C. Proceed with derivatization.

C. Cotton Gloves.

Note: Gloves have to be washed and dried prior to use to remove most of the lint which will leave a residue when dried and cause difficulties in the derivatization reaction.

- 1. Place gloves in a mason jar with 250 ml methanol.
- 2. Shake on a gyratory shaker at 150 rpm for 30 min.
- 3. Transfer 100 ml of the methanol extract to a 250-ml boiling flask and evaporate to about 2 ml.
- 4. Filter condensed extract through a nylon acrodisc (0.2 um) filter into a 15-ml glass stoppered test tube. Rinse the boiling flask by sonicating with methanol and pass the rinsing through the same filter into the test tube.
- 5. Evaporate to dryness under N_2 at $50\text{-}60^{\circ}\text{C}$ and proceed with the derivatization reaction.

D. Handwashes

- 1. Measure total volume of handwash and transfer half of the volume to a separatory funnel. Add 30 g NaCl and shake to dissolve.
- 2. Extract with 2 x 50 ml ethyl acetate. Combine extracts in a 100-ml

- graduated cylinder and adjust volume to 100-ml with ethyl acetate.
- 3. Add anhydrous Na2SO4 to the cylinder and shake.
- 4. Measure out 50 ml of the ethyl acetate extract into a boiling flask and evaporate to near dryness.
- 5. Transfer concentrated extract to a 15-ml glass stoppered test tube. Rinse boiling flask by sonicating with a few mls of methanol. Add rinsing to test tube.
- 6. Evaporate to dryness under N_2 at $50\text{-}60^{\circ}\text{C}$ and proceed with derivatization.

E. Dislodgeable Residues

- Add 50 mls distilled water and 3-4 drops Sur-Ten solution to the leaf punches in sample jar. Rotate for 30 min.
- Repeat above procedure two more times and combine aqueous strip in a separatory funnel.
- 3. Add 20-30 g NaCl to the funnel and shake to dissolve. Proceed as with handwashes starting with step No. 2.

Derivatization Reaction:

- Add 0.1 ml of derivatizing reagent to the dried extract in the test tube. For gauzes, gloves and handwashes, use 0.3 ml of the reagent (see Discussion A.). Vortex and sonicate for one minute.
- 2. Tape stopper to tube and place in a heating block or oil bath (95- 100° C) for one hour.
- 3. The reaction mixture should turn black after heating. If otherwise, discard and repeat the procedure with the remaining half of the sample extract.
- 4. Allow tubes to cool. Add 1 ml CHCl3, vortex and sonicate for one minute.
- 5. Prewash a Sep-Pak silica cartridge with 5 ml CHCl₃. Pass reaction mixture through the Sep-Pak and collect eluant in a 15-ml test tube. Rinse original tube with 3 x 1 ml CHCl₃ and pass rinsings through the Sep-Pak. Elute with additional CHCl₃ to give a final volume of 13 ml.
- Evaporate to dryness under N₂ at 50-60°C.
- 7. Dissolve residue in 2 ml methanol using sonication. Sample is ready for liquid chromatography.
- 8. A set of standard avermectin solutions is derivatized with each batch of test samples.

CALCULATIONS:

The amounts of avermectin B_{1a} in the test samples are calculated from the linear regression curve of peak height vs. concentration of the standard solutions derivatized with the test samples. In our study, the peak heights of standard solutions had coefficients of variation of 5-8%. Recoveries from spiked samples were close to 100% at levels of 35, 175 and 700 ng.

DISCUSSION:

A. Derivatization Reaction

It was found necessary to increase the amount of derivatizing reagent from 0.1 ml to 0.3 ml for the extracts of gauzes, gloves and handwashes due apparently to the presence of other dissolved substances which consume the reagent. The use of less than 0.3 ml of

reagent cause either a failure of the reaction to occur, as seen from the absence of the black color after heating, or an incomplete reaction, as shown by low recoveries from spiked samples. Standard solutions of avermectin, when derivatized using 0.3 ml of reagent gave no increase in reaction yields over those obtained using 0.1 ml.

Extracts of cloth patches, air filters and XAD-4 resin tubes were relatively clean and needed only 0.1 ml of reagent.

Critical factors for the reaction are: temperature, which should be at least 95° C, and the complete absence of any moisture in the reaction tube(2).

The avermectin derivative was stable in refrigerated storage for at least one month.

B. Chromatography

Retention time was sensitive to very slight changes in the water content of the mobile phase. Premixing of mobile phase gave more consistent results than pump mixing. To achieve good reproducibility of retention time between batches of premixed mobile phase, the water had to be measured by pipet into a volumetric flask and methanol added to volume.

Avermectin B_1 derivative had a retention time of 8.17 min and a minimum detectable amount of 0.2 ng.

REFERENCES:

- 1. "HPLC-Fluorescence Determination of Avermectin B₁ in Worker Exposure Sampling Media", Method No. 5004, Merck Sharp & Dohme Research Laboratories, Three Bridges, New Jersey, 1986.
- 2. Teresa A. Wehner, Merck Sharp & Dohme Research Laboratories, personal communications, 1987.

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APPENDIX II

TABLE VI: Locations of Dermal Exposure Pads and Body Surface Areas for Each Body Region.

PATCH	LOCATION	SURFACE AREA	AREA REPRESENTED	CONVERSION a_ FACTOR_
Head		1300.0	Head, including face	27.36
Back		3660.0	Back; back of neck	77.02
Chest		3700.0	Chest/Stomach, front of neck	77.86
Bicep		2910.0	Shoulder, upper arm	61.24
Forearm	-front	605.0	Front forearm	12.73
	-rear	605.0	Rear forearm	12.73
Thigh	-front	1910.0	Front thigh	40.19
	-rear	1910.0	Rear thigh	40.19
Shin	-front	1190.0	Front lower leg	25.04
٠ .	-rear	1190.0	Rear lower leg	25.04

Body surface area = conversion factor
Surface area of two patches

¹⁾ Source: Environmental Protection Agency, Pesticide Assessment Guidelines, Subdivision U, Applicator Exposure Monitoring (4)